



SL IB Chemistry



Your notes

Electron Pair Sharing Reactions

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- * Nucleophilic Substitution
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Your notes

Nucleophilic Substitution

Nucleophilic Substitution

What is a nucleophile?

- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
 - 'Nucleophile' means 'nucleus/positive charge loving' as nucleophiles are attracted to positively charged species
 - Nucleophilic** refers to reactions that involve a nucleophile
- There are various different species which can behave as nucleophiles, and some make better nucleophiles than others



A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge

Examples of neutral and charged nucleophiles

Neutral	Charged
H ₂ O	OH ⁻
NH ₃	Cl ⁻
ROH	CN ⁻
RNH ₂	R ⁻ (carbanions)

- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile

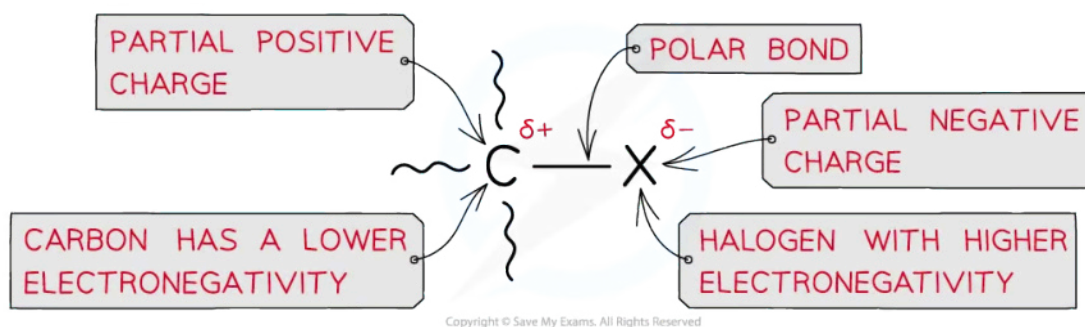


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Equations for Nucleophilic Substitution

- Haloalkanes will undergo nucleophilic substitution reactions due to the polar C-X bond (where X is a halogen)

Partial positive C atom and partial negative X atom



Due to large differences in electronegativity between the carbon and halogen atom, the C-X bond is polar

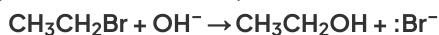
Diagram to show nucleophilic substitution where $:\text{Nu}^-$ represents the nucleophile



General Mechanism for Nucleophilic Substitution

Hydrolysis of Haloalkanes

- The nucleophile in this reaction is the hydroxide, OH^- ion
- An **aqueous** solution of **sodium hydroxide** (NaOH) or **potassium hydroxide** (KOH) with **ethanol** is used
- This reaction is very slow at room temperature, so the reaction mixture is warmed
- This is an example of a **hydrolysis reaction** and the product is an alcohol



- $:\text{Br}^-$ is the leaving group
 - Halogens make good leaving groups as they form relatively weak bonds with carbon
 - Their higher electronegativity also means the bonded electrons are drawn towards the halogen atom making the carbon partially positive, $\delta+$, and susceptible to nucleophilic attack
- The rate of this reaction depends on the type of halogen in the haloalkane

- The stronger the C-X bond, the slower the rate of the reaction
- In terms of bond enthalpy, C-F > C-Cl > C-Br > C-I
- Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction

The nucleophilic substitution mechanisms for the above reactions are as follows:

Nucleophilic substitution mechanism of bromoethane with a hydroxide ion

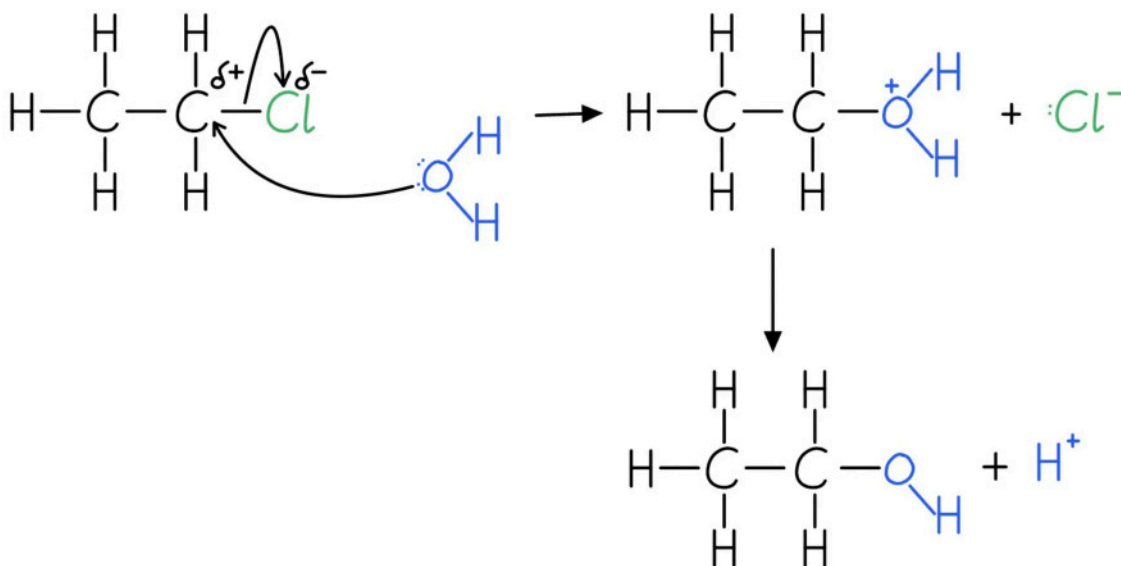


Nucleophilic Substitution with OH^- , the bond that forms and the bond that breaks must both involve the carbon atom that is bonded to the leaving group

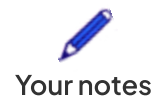
Neutral nucleophiles

- When the nucleophile is neutral, e.g. H_2O , the initial product is positive
- The positive product then deprotonates, losing H^+ , and forms a neutral product
 - $\text{CH}_3\text{CH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+$

Diagram to show water acting as a nucleophile forming a positive product which is then deprotonated



Nucleophilic substitution reactions with neutral nucleophiles involves deprotonation





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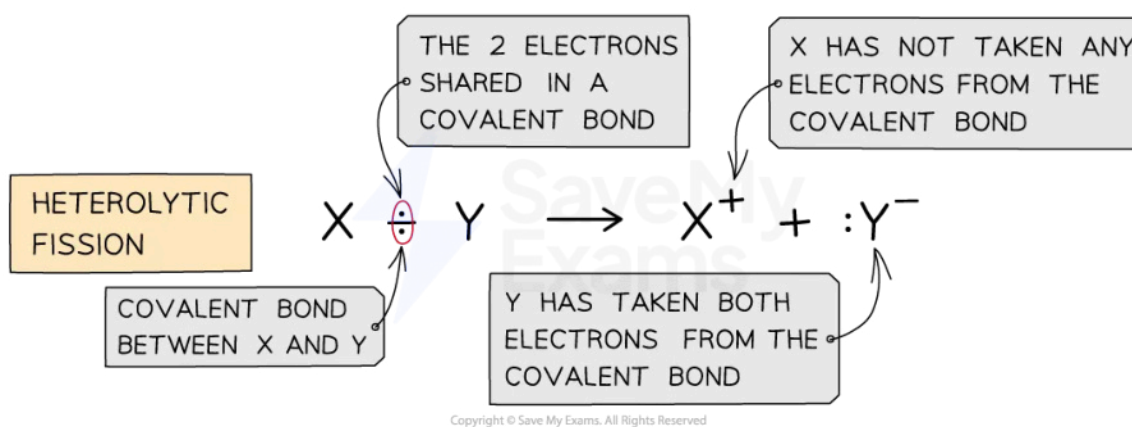
Heterolytic Fission

Heterolytic Fission

Heterolytic fission

- Heterolytic fission is breaking a covalent bond in such a way that the more electronegative atom takes both the electrons from the bond to form a negative ion and leaves behind a positive ion

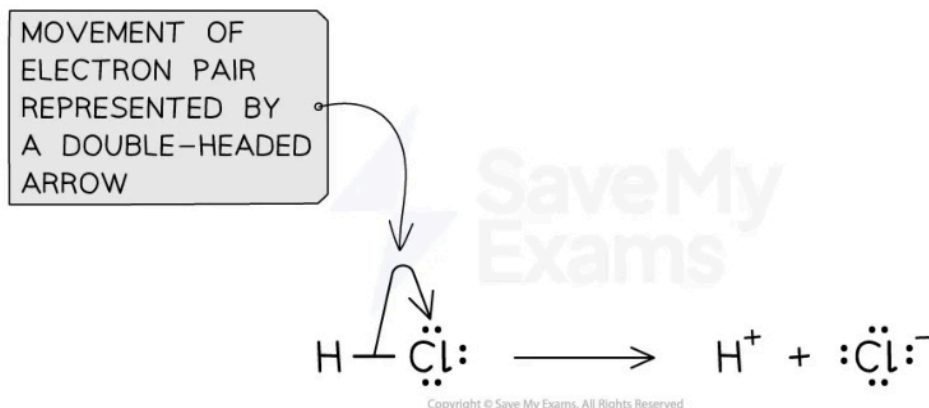
Diagram to show the process of heterolytic fission



Heterolytic fission forms a positive ion and a negative ion

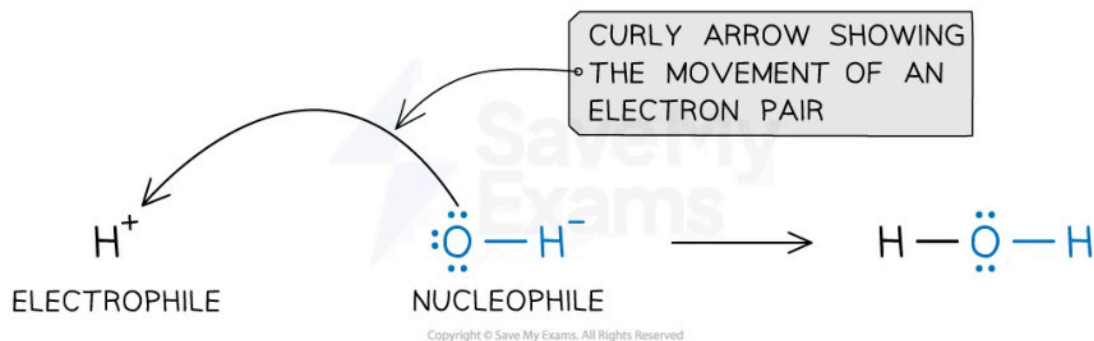
- In heterolytic fission, a double-headed arrow is used to show the movement of a **pair of electrons**
- The resulting negative ion is an electron-rich species that can **donate** a pair of electrons
 - This makes the negative ion a **nucleophile**
- The resulting positive ion is an electron-deficient species that can **accept** a pair of electrons
 - This makes the positive ion an **electrophile**

Heterolytic fission mechanism



- The opposite reaction to heterolytic fission occurs when a nucleophile donates a pair of electrons to the electrophile forming a coordination bond

Reaction between a nucleophile and an electrophile forming a coordination bond



A nucleophile 'loves' a positive charge and an electrophile 'loves' a negative charge



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Electrophilic Addition Reactions

Electrophiles

What is an electrophile?

- An electrophile is a species that forms a covalent bond when reacted with a nucleophile by accepting electrons
- They are electron-deficient so will have a positive charge or partial positive charge

Examples of neutral and charged electrophiles

Neutral	Charged (cations)
HX (hydrogen halides)	H^+
X_2 (halogens)	NO_2^+
H_2O	NO^+
RX (halogenoalkanes)	R^+



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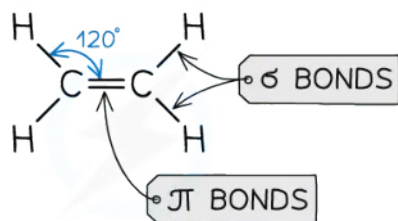
Electrophilic Addition Reactions

- **Electrophilic addition** is the addition of an electrophile to an alkene double bond, C=C
- The alkene double bond, C=C, is an area of high electron density which makes it susceptible to attack by electrophiles
- The C=C bond breaks forming a single C-C bond and 2 new bonds from each of the two carbon atoms
- Electrophilic addition reactions include the addition of:
 - Steam, H₂O (g) to form alcohols
 - Hydrogen halides, HX, to form halogenoalkanes
 - Halogens, X₂, to form dihalogenoalkanes

Why does the C=C bond react with electrophiles?

- Alkenes are unsaturated molecules that contain a C=C bond
- The atoms around the carbon-carbon double bond adopt a **planar arrangement** and the bond angle is 120°

Diagram to show the planar arrangement of the C=C bond

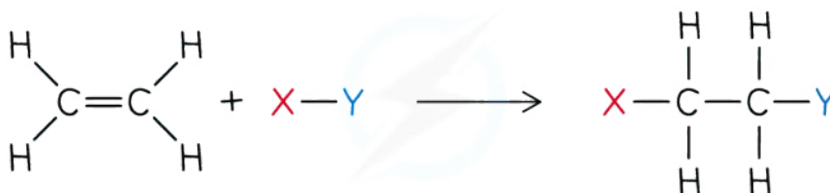


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The bond angles are 120°

- The presence of the C=C bond gives **alkenes** a number of chemical properties that are not seen in **alkanes**
- Since the **alkene** contains **π-bonds**, it is possible to break the weaker **π-bond** and form stronger **σ-bonds** with other species without forcing any atoms on the molecule to break off
- As a result **alkenes** (unlike **alkanes**) are capable of undergoing **addition reactions**
- The ability of **alkenes** to undergo **addition** means that they are much **more reactive** than **alkanes**

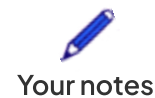
Diagram to show the general equation for addition reactions across the C=C



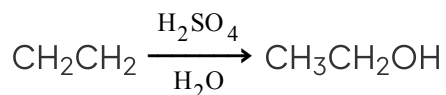
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Addition reactions in alkenes

Addition of water



- When alkenes are treated with steam at **300 °C**, a pressure of **60 atmospheres** and **sulfuric acid (H₂SO₄)** or **phosphoric acid (H₃PO₄)** catalyst, the water is added across the double bond in a reaction known as **hydration**
- An **alkene** is converted into an **alcohol**
- The reaction processes via an intermediate in which H⁺ and HSO₄⁻ ions are added across the **double bond**
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid
- The following equation shows the conversion of ethene to ethanol



ethene ethanol

- This is a very important industrial reaction for producing large quantities of ethanol, a widely used solvent and fuel
- The process is much faster and higher yielding than producing ethanol by **fermentation**

Addition of halogens

- The reaction between **alkenes** and halogens is known as **halogenation**
- It is an example of an **electrophilic addition** where an electrophile ('electron seeker') joins onto to a double bond
- The C=C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- The result of this reaction is a **dihaloalkane**

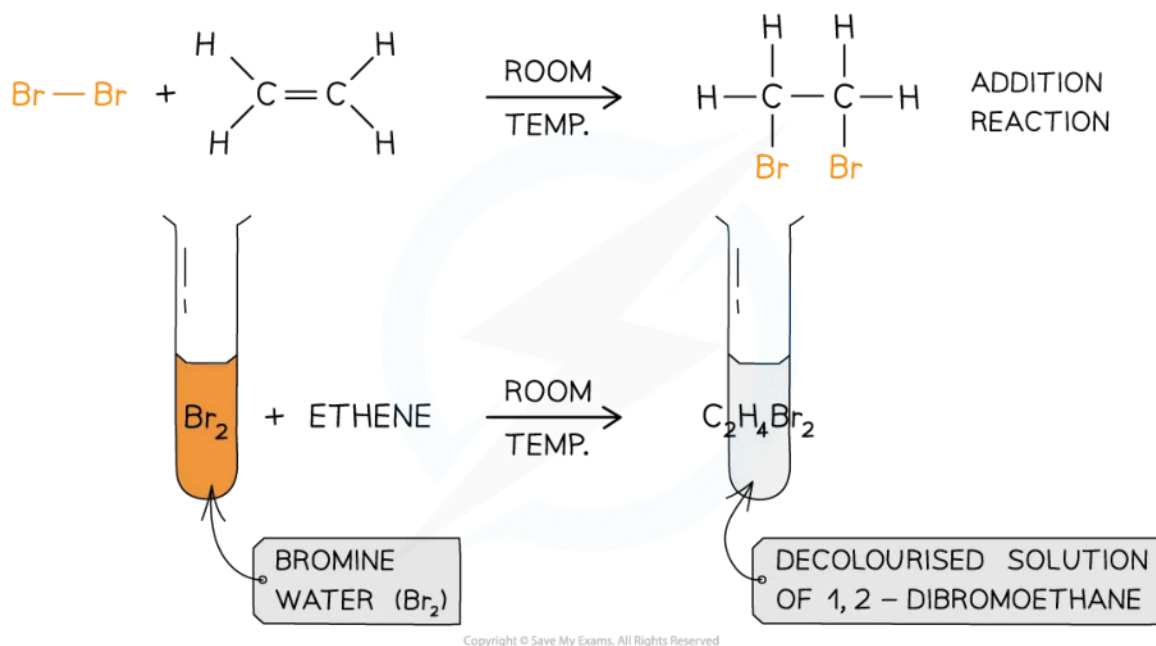
This reaction occurs readily at room temperature and is the basis for the test for unsaturation in molecules



Halogenation in alkenes

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br₂ is an orange or yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise

Diagram to show the colour change that occurs when testing for unsaturation



The bromine water test is the standard test for unsaturation in alkenes

Addition of hydrogen halides

- Alkenes will react readily with **hydrogen halides** such as **HCl** and **HBr** to produce **halogenoalkanes**
- This reaction is known as **hydrohalogenation**
- It is also an **electrophilic addition** reaction that occurs quickly at room temperature

Formation of a halogenoalkane from an alkene and hydrogen halide



Hydrohalogenation reactions in alkenes

- All the **hydrogen halides** react in this way, but the **fastest reaction** occurs in the order **HI > HBr > HCl** due to the increasing bond strength of the hydrogen-halogen bond, so the weakest bond reacts most easily